



ADDENDUM

**Agency Interpretive Report for
MBMG's ARWW&S Arsenic Source Investigation
Final Project Data Summary Report,
dated 10-31-2013**

**CDM
Smith**

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Section 1

Introduction

1.1 Summary of Interpretive Report

The Agency Interpretive Report (CDM Smith 2014) used oxygen, deuterium, and sulfur stable isotopes, total arsenic within rock cores, soil, and sediment and synthetic precipitation leaching procedure (SPLP) leaching results on rock, soil, and sediment provided within MBMG's Data Summary Report (DSR) (MBMG 2013) to evaluate the conclusions drawn within Atlantic Richfield's (AR's) "Draft Arsenic Source Investigation Interpretive Analysis" report (AR 2013). The AR report focused almost entirely on multivariate statistical analyses of the groundwater data and will be referred to hereafter as "AR's statistical report." The Agency Interpretive Report concluded that (1) some arsenic in ground water was derived from bedrock sources within specific areas (Crackerville Deep and English Gulch); (2) ground water associated with geothermal areas contained less than 30 µg/L arsenic; and (3) ground water associated with geothermal areas was very limited in horizontal extent. There was no evidence for widespread geothermal or bedrock sources of arsenic to the ground water. The only source that was consistent with the data was smelter fallout. The surface soils (0-6 inches) were very leachable and the tritium data indicated that meteoric or surface water from the 1950s was present at depths of up to 300 feet (such as in the Powell Vista area). The predominant wind directions to the north and southeast were consistent with the high surface concentrations of arsenic and arsenic within groundwater and supported an expansion of the monitoring boundary.

1.2 Purpose of the Addendum

This Addendum to CDM Smith's Interpretive Report for MBMG's ARWW&S Arsenic Source Investigation was prepared to address some of the comments received from AR (EnSci, Inc, dated June 22, 2014). The addendum will focus on the following:

- Trace element (W, Rb, Cs, etc.) evaluation
- Smelter fallout extent and AR's proposed 6 mile radius and 35 foot depth limit of groundwater smelter impacts

The addendum will not cover sulfur isotopes or the issues associated with the use of temperature within the statistical analysis. AR's objection to the range of sulfur isotope values used for smelter fallout and abiogenic sulfide has been adequately addressed in our response to comments. AR has agreed to remove temperature from the revised statistical analysis to be performed by AR at a later date.

Section 2

Trace Element Evaluation

The alleged relationship between arsenic and trace metals such as tungsten, boron, lithium, rubidium, and cesium will be further evaluated. AR contends that the alleged relationship between arsenic and the trace elements is evidence for a “geothermal” source of arsenic within the ARWW&S ground waters. In CDM Smith’s Interpretive Report, it was clearly shown that the arsenic concentrations within the geothermal wells were insufficiently high ($<30\mu\text{g/L}$) to explain the observed arsenic levels in groundwater either within or outside of AR’s proposed 6 mile radius of influence for the smelter emissions. AR’s comments on CDM Smith’s Interpretive Report regarding trace elements from rock core leachate seem to suggest that AR is proposing paleo-geothermal deposits or possibly hydrothermal alteration zones as a source. AR has often used “geothermal” and “hydrothermal” interchangeably, further confusing the issue. For instance, on page 5 of AR’s statistical report is a list of elements which comprise a “high pH geothermal system” and references Barnes, 1979. However, Barnes (1979) is a book on hydrothermal ore deposits (*Geochemistry of Hydrothermal Ore Deposits*). Lindgren (1933) defined hydrothermal deposits as “ores formed by hot, aqueous solutions” which he subdivided into four categories;

Hypothermal – Deposits formed at great depth and at high temperature (300-500 °C)

Mesothermal – Deposits formed at intermediate depths and temperatures (200-300 °C)

Epithermal – Deposits formed at shallow depths and relatively low temperatures (50-200 °C)

Hydrothermal solutions consist of hot brines which contain high metals concentrations as chloride, sulfide, or other aqueous complexes (Gilbert and Park 1986). Hydrothermal solutions can be magmatic, sea water, meteoric (derived from local ground water), or a mixture of water types (Gilbert and Park, 1986).

Geothermal waters have elevated temperatures which can overlap with the temperatures of epithermal waters, but in Montana they generally have a different source. Geothermal waters consist of warm groundwater which is derived almost entirely from local precipitation (Richardson and McSween 1989). Most of the geothermal waters in southwest Montana are derived from deep circulation of ground water rather than a cooling igneous body (USGS 1979). The thermal waters occur in deeply fractured crystalline rock or within Cenozoic block fault valleys underlain and surrounded by crystalline rock or both (USGS 1979). Both the Fairmont and Warm Springs areas overlie known or inferred major valley margin faults. The deep circulation along fault zones results in heating of the water in areas of normal geothermal gradients as opposed to an igneous heat source which would have an anomalously high geothermal gradient. Based on the geothermal gradient of valley fill material, the ground water would need to circulate to depths of about 1 km to reach a temperature of 60°C. Geothermometry studies have shown that the Warm Springs thermal waters are derived from a low temperature reservoir and not from cooling of warmer water (USGS, 1976). Fairmont is believed to issue from a low temperature aquifer (110-150°C), which has cooled during the ascent to the surface (USGS 1976).

Some geothermal waters (60 °C) can have relatively high levels of arsenic (As), boron (B), molybdenum (Mo), vanadium (V), potassium (K), silicon (Si), dissolved organic carbon (DOC), phosphorous (P), fluoride (F) and pH (Bonteet *al.* 2013). These elements are derived from either dissolution of minerals or, in the case of arsenic, desorption processes (Bonteet *al.* 2013). Most mineral dissolution and desorption reactions are enhanced at higher temperatures. When these waters cool to below 25°C the re-adsorption of arsenic would occur. In effect, geothermal waters are not a source of arsenic, but a means of transporting arsenic that is already present within the system.

The distinction between modern geothermal waters and hydrothermal deposits may at first seem trivial, but they are completely different processes. The former relates to the enhanced leaching ability of warm local ground water, and the latter to deposits formed millions of years ago in relation to the emplacement of igneous rocks. The trace elements which will be discussed in the following sections often occur in both geothermal waters and hydrothermal deposits, but can also occur in pegmatites and felsic volcanics. The distribution of both mineralized bedrock and geothermal water, as described in the interpretive report, are very limited at ARWW&S, occurring in very specific areas. The evaluation and discussion will include tungsten, boron, and the “rare” alkali metals rubidium, lithium, and cesium.

2.1 Tungsten (W)

Tungsten (W) is a transition metal and is in group VI of the periodic table along with chromium (Cr) and molybdenum (Mo). W exists in oxidation states of 0, +2, +3, +4, +5 and +6, but only the +6 oxidation state is important in natural waters. W(+6) exists predominantly as the oxyanion WO_4^{2-} at neutral to alkaline pH values (7-9).

2.1.1 Occurrence

W occurs mainly within the scheelite and wolframite groups of minerals. The scheelite group consists of the solid solution series $Ca(WO_4, MoO_4)$, while the wolframite group consists of the $(Fe, Mn)WO_4$ solid-solution series. The scheelite group is the most common and occurs within late stage granitic rocks, high temperature hydrothermal veins within granite, and pegmatite deposits. Tungsten rich hot springs deposits have been mined for W near Golconda, NV (Seiler *et al.* 2005). W can also be present within secondary phases such as iron oxyhydroxides.

W within natural water at concentrations in excess of ~9 ug/L is generally derived from one of four sources (Seiler *et al.* 2005):

1. Groundwater associated with W-bearing ore deposits
2. Alkaline, nitrogenous fissure-vein thermal waters of crystalline rocks
3. Alkaline waters of lakes in arid areas
4. Hot spring waters and hydrothermal vents

W from anthropogenic (manmade) sources includes phosphate fertilizers. Seiler *et al.* (2005) state that commercial phosphate fertilizers contain from 1.2 to 7.8 mg/kg W.

2.1.2 Distribution at the Site

A summary of some W analyses within various water types, including some of the site waters, is presented in **Table 2-1**.

Table 2-1 – Summary of Tungsten Occurrence in Waters

Water	Tungsten (ppm)
Brines	
Searles Lake, CA ¹	~49
Geothermal Springs	
Walker River Basin, CA ¹	0.0026 – 0.332 (the three highest from hot springs with temperatures >38°C)
Hot Springs ¹	1 – 1,000
Warm Springs Hospital ²	0.0062
Fairmont Springs ²	0.301-0.322
Geyser Gulch (active and dormant geysers) ²	0
Groundwater	
Carson Desert, NV Drinking Water Aquifer ¹	0.00027 – 0.742
Walker River Basin, CA ¹	0.008 – 0.128
Jean and Elden Fresh Well ²	0.1797
Median Anaconda Groundwater ²	0.000155

1. Seiler *et al.* (2005)

2. Using AR database provided with the Statistical Report

Potential W-bearing source rocks within the area include granitic rocks (Boulder Batholith) and associated veins and pegmatites, volcanic rocks (Lowland Creek), and vent deposits.

Some W sources also contain As. Seiler *et al.* (2005) found a strong and positive correlation between As and W within the groundwater near Fallon, NV. However, they attribute the correlation, in part, to reductive dissolution of secondary iron oxyhydroxides, which can contain W and As derived from different original sources.

SPLP leaching results (MBMG 2013) for arsenic and tungsten are presented in **Table 2-2**.

Table 2-2 – Arsenic and Tungsten SPLP Leaching Results¹

Rock Sample	Type	As	W
English Gulch (RW)	Rock	9051.99	<0.1
Crackerville (FR)	Rock	522.03	129.98
Tlcl Breccia	Rock	12.64	0.67
Crackerville (FR)	Rock	4.82	5.81
English Gulch (RW)	Rock	55.1	0.45
English Gulch (RW)	Rock	20.37	<0.1
Fairmont (SH)	Rock	15.15	2.02
Fairmont (SH)	Rock	8.3	5.25
Kg-Granite weathered	Rock	17.24	<0.1
Tlcl Apanitic	Rock	0.69	<0.1
Tlcl Lava	Rock	0.89	<0.1
Tlcp Porphyry (Lowland Creek)	Rock	18.66	0.29
Tlcw Welded Tuff (Lowland Creek)	Rock	12.77	<0.1
Tuxedo Mine Red-black breccia	Rock	0.45	<0.1

Table 2-2 – Arsenic and Tungsten SPLP Leaching Results¹

Rock Sample	Type	As	W
Tuxedo Mine yellow-gray breccia	Rock	2.31	<0.1
Crackerville (FR)	Sediment	14.57	33.18
Fairmont (SH)	Sediment	0.87	13.37
Powell Vista (MS)	Sediment	7.48	7.55
Powell Vista (MS)	Sediment	19.6	87.78
Powell Vista (MS)	Sediment	16.02	33.27
Crackerville (FR)	Soil	118.59	3.22
English Gulch (RW)	Soil	89.08	0.23
Fairmont (SH)	Soil	218.14	0.33
Fairmont (SH)	Soil	220.37	0.34
Fairmont (SH)	Soil	221.88	0.38
Powell Vista (MS)	Soil	448.91	0.43
Soil near Flint Creek Area	Soil	185.4	0.26
Soil near MW-229	Soil	106.41	0.25

1. MBMG (2013) Tables 7 and 8

Some samples leached both arsenic and tungsten, such as the core sample collected at 118 m from Crackerville (533 ug/L As and 130 ug/L W). Others, such as the sample collected at English Gulch at 41 m do not (9,052 ug/L As <0.1 ug/L W). Plot of As vs. W with and without the Crackerville and English Gulch samples are presented in **Figures 2-1a and 2-1b**.

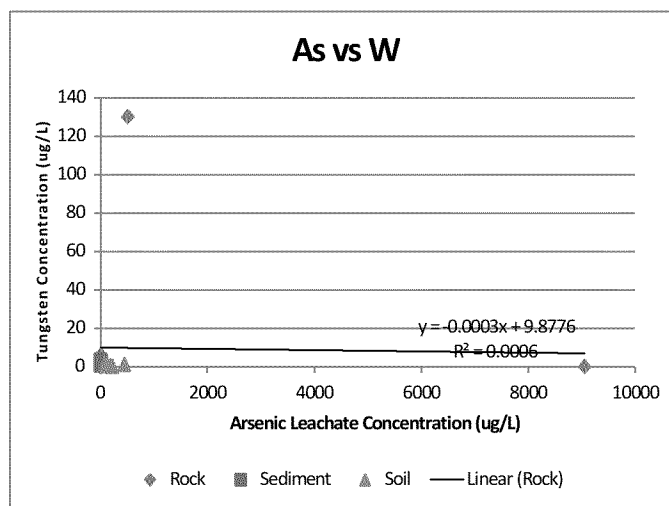


Figure 2-1a – As vs W in SPLP leachate (all samples).

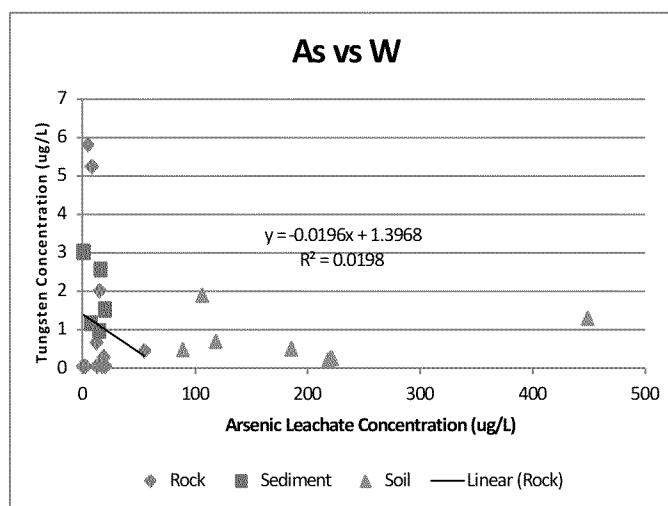


Figure 2-1b – As vs W in SPLP leachate (without English Gulch 41 m or Crackerville 118 m).

The correlation for the rock samples is very poor ($R^2 = 0.0006$ to 0.02), which suggests that there is more than one source of tungsten at the site, the arsenic and tungsten are not from the same source, or the geochemical conditions for mobilization of W and As are different.

Figure 2-2 – W on geologic map

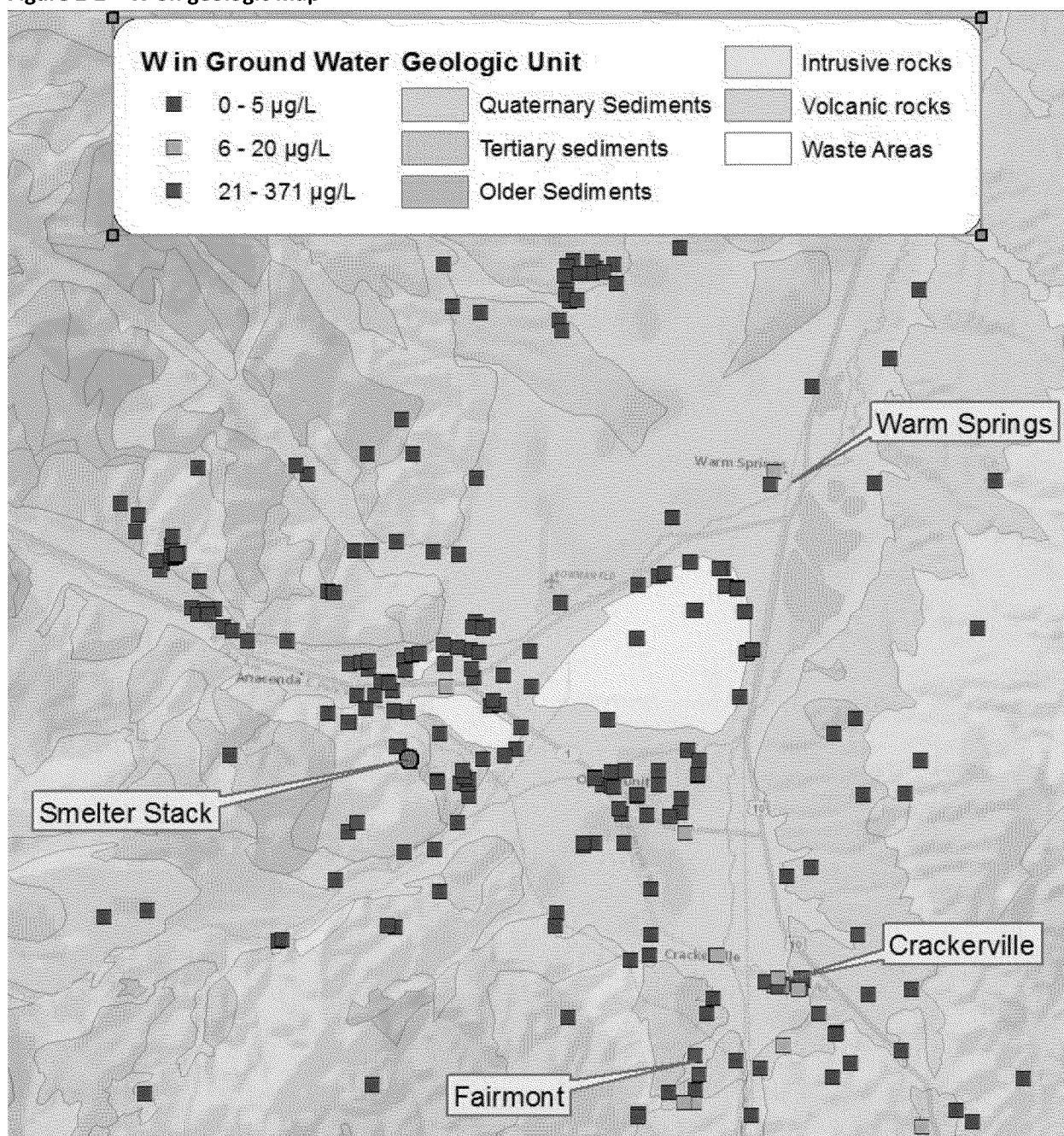


Figure 2-2 shows the spatial distribution of tungsten in groundwater at the site superimposed on a geologic base map. The tungsten concentrations do not appear to correlate with any given rock type but are fairly randomly distributed across the site.

A plot of As vs. W in groundwater (limited to As < 50 µg/L) shows that there is no correlation between the two parameters (see **Figure 2-3**). Arsenic concentrations ≥ 50 µg/L were excluded to avoid the effect of samples which are clearly associated with mine waste or smelter emissions.

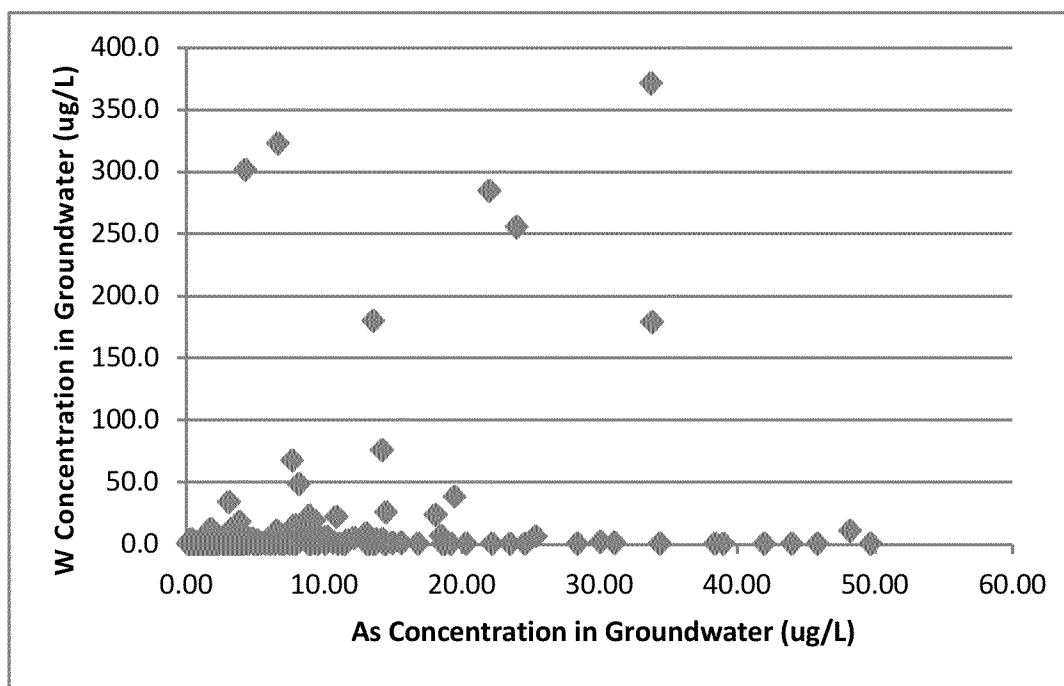


Figure 2-3 – As vs W concentrations in site groundwater (limited to As < 50 µg/L).

Clearly, there is no correlation between W and As in site groundwater. In fact, most of the samples with As concentrations between 10 and 50 µg/L are not accompanied by high W concentrations.

Multiple lines of evidence show that W cannot be used as a practical guide for predicting the source or sources of arsenic at the site.

2.2 Boron (B)

Boron is in group IIIA of the periodic table in the same group as aluminum. Boron, like aluminum, exists only in the +3 valence state. In solution, the dominant species is boric acid ($B(OH)_3$). Boric acid can hydrolyze to form $B(OH)_4^-$, which predominates above a pH of 9.24.

2.2.1 Occurrence

Boron is commonly present within granitic rocks and the minerals tourmaline $[(Na,Ca)(Mg,Li,Al,Fe^{2+})_3(Al,Mg,Cr)_6(BO_3)_3Si_6O_{18}(OH)_4]$, biotite $(K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2)$, and amphiboles such as hornblende $(Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2)$ (Hem 1985). Boron also occurs within fly ash from coal fired power plants and other facilities that burn coal. Leachate from fly ash repositories can reach over 100 mg/L.

Geothermal waters outside of Montana are on the order of 10-70 mg/L, but most of the hot springs within Montana have concentrations of 0.1 – 0.5 mg/L.

Table 2-3 – Summary of Boron Occurrence in Waters

Water	Boron (ppm)
Brines	
Great Salt Lake	-
Salton Sea	400-500
Geothermal Springs	
Steamboat Springs, CO	67.5
Steamboat Springs, NV	49.0
Yellowstone	11.5
Alhambra Hot Springs	0.24
Boulder Hot Springs - a	0.54
Boulder Hot Springs - b	0.56
Pipestone Hot Springs	0.28
Warm Springs Hospital	0.11
Fairmont Springs	0.25-0.32
Geyser Gulch	0.09-0.10

2.2.2 Distribution at the Site

Boron can occur within the granitic rocks in the ARWW&S area, within pegmatites, and clay minerals within the aquifer. The pegmatites in Montana which are within or proximal to the Boulder Batholith are known to contain tourmaline (Heinrich 1949).

The leaching results for B and As obtained by MBMG are provided in **Table 2-4**.

Table 2-4 - Arsenic and Boron SPLP Leaching Results¹

Rock Sample	Type	As	B
English Gulch (RW)	Rock	9051.99	244.5
Crackerville (FR)	Rock	522.03	100.88
Tlcl Breccia	Rock	12.64	5.22
Crackerville (FR)	Rock	4.82	8.01
English Gulch (RW)	Rock	55.1	2.65
English Gulch (RW)	Rock	20.37	0.56
Fairmont (SH)	Rock	15.15	15.65
Fairmont (SH)	Rock	8.3	15.48
Kg-Granite weathered	Rock	17.24	2.51
Tlcl Apanitic	Rock	0.69	4.32
Tlcl Lava	Rock	0.89	1.33
Tlcp Porphyry	Rock	18.66	7.46
Tlclw Welded Tuff	Rock	12.77	4.76
Tuxedo Mine Red-black breccia	Rock	0.45	5.83
Tuxedo Mine yellow-gray breccia	Rock	2.31	0.73
Crackerville (FR)	Sediment	14.57	38.38
Fairmont (SH)	Sediment	0.87	19.99
Powell Vista (MS)	Sediment	7.48	23.78
Powell Vista (MS)	Sediment	19.6	18.24

Table 2-4 - Arsenic and Boron SPLP Leaching Results¹

Rock Sample	Type	As	B
Powell Vista (MS)	Sediment	16.02	10.45
Crackerville (FR)	Soil	118.59	37.89
English Gulch (RW)	Soil	89.08	10.98
Fairmont (SH)	Soil	218.14	11.08
Fairmont (SH)	Soil	220.37	11.12
Fairmont (SH)	Soil	221.88	12.72
Powell Vista (MS)	Soil	448.91	10.58
Soil near Flint Creek Area	Soil	185.4	12.31
Soil near MW-229	Soil	106.41	7.36

1. MBMG (2013) Tables 7 and 8

The two highest arsenic leachate concentrations (English Gulch 41 m and Crackerville 118 m) correspond with the highest B concentrations. Plots of As vs. B for the SPLP leachates is provided in **Figures 2-4a** and **2-4b**.

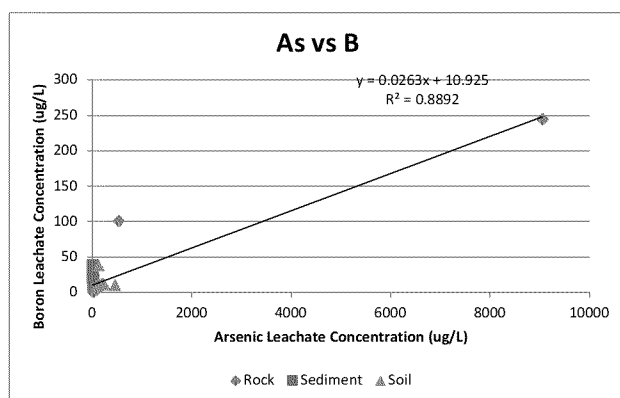


Figure 2-4a - As vs B in SPLP leachate (all samples).

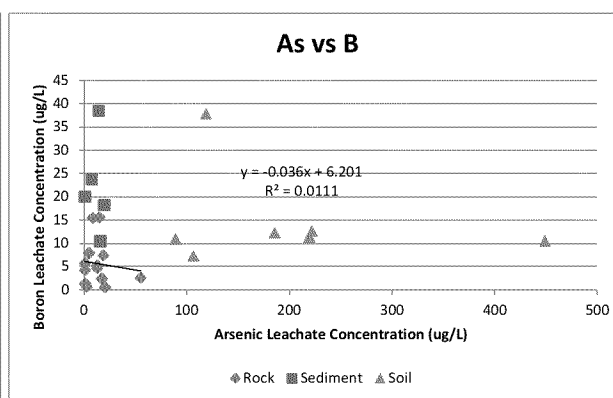
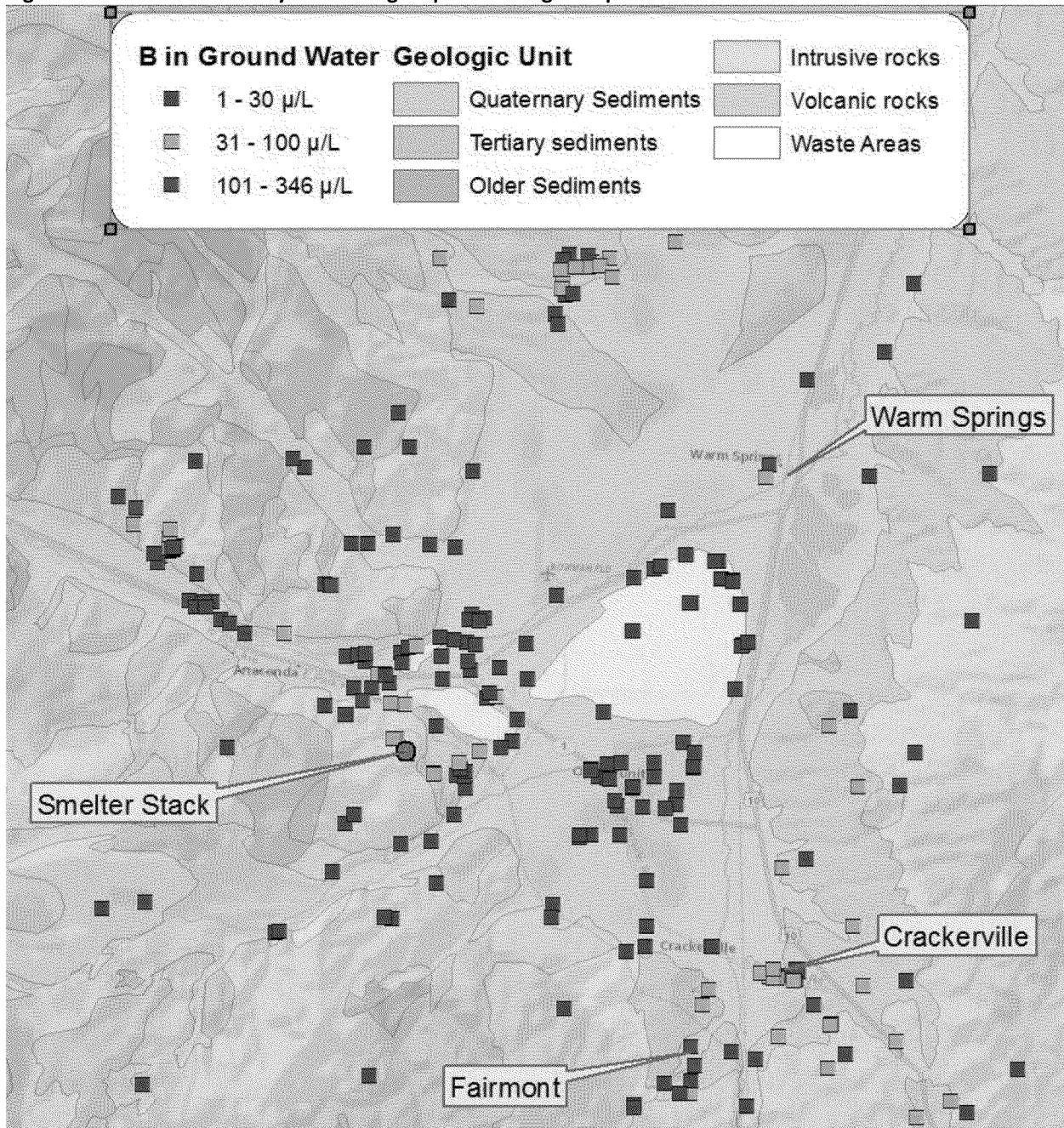


Figure 2-4b - As vs B in SPLP leachate (without English Gulch 41 m or Crackerville 118 m).

On first inspection, there appears to be a rough correlation between As and B. The Rsquared was 0.88 (**Figure 2-4a**). However, with the exception of two points (English Gulch 41 m and Crackerville 118 m) all of the data plot in a cluster near the origin of the graph. When these two points are removed (**Figure 2-4b**) the correlation falls apart ($R^2 = 0.01$).

Figure 2-5 - B distribution by Chatham group on Geologic map



A plot of As vs B for the ground water in which As < 50 µg/L is presented in **Figure 2-6**.

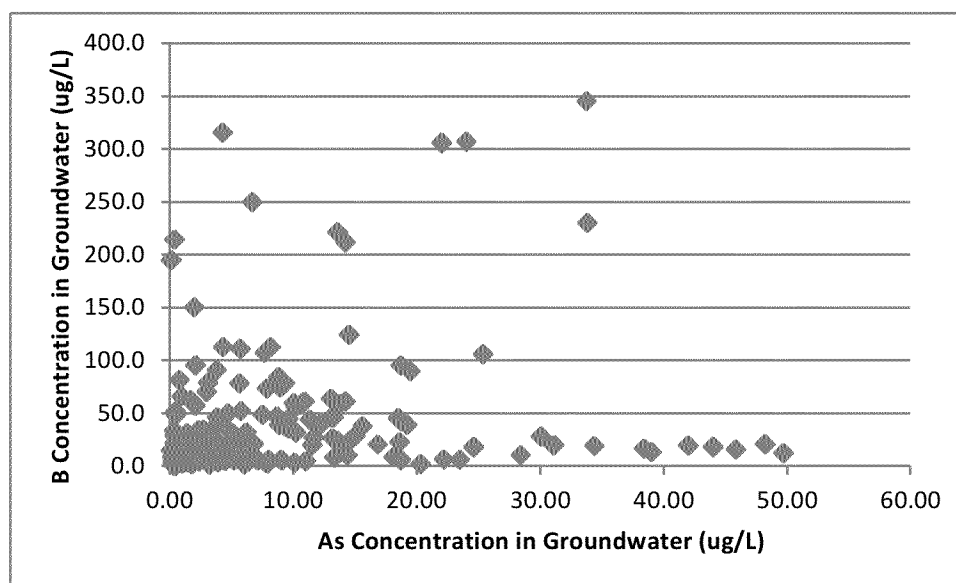


Figure 2-6 - As vs B concentrations in site groundwater (limited to As < 50 µg/L).

The correlation is poor, illustrating that As and B do not have a common source, or there are multiple sources of B present.

2.3 Rare Alkali Metals

The rare alkali metals include lithium (Li), rubidium (Rb) and cesium (Cs), all within group IA of the periodic table. Other members of group IA include sodium and potassium, which are far more common.

2.3.1 Occurrence

Lithium occurs within the minerals spodumene ($\text{LiAl}(\text{Si}_2\text{O}_6)$), amblygonite ($(\text{Li},\text{Na})\text{Al}(\text{PO}_4)(\text{F},\text{OH})$), and lepidolite mica ($\text{K}_2\text{Li}_3(\text{OH},\text{F})_4(\text{AlSi}_3\text{O}_{10})_2$), all of which occur predominantly within pegmatites (Hem, 1985). Lithium occurs within some clay minerals (hectorite, Li-stevensite, Li-smectite, etc.) with concentrations as high as 0.7% (Garrett 2004). Lithium is also found within natural brines, such as at Searles Lake, CA.

Rubidium is more abundant than lithium, but there are no pure phase rubidium minerals. Rb tends to substitute for potassium within minerals and is more strongly held by the cation exchange sites within clay minerals than lithium (Hem 1985).

Cesium is rarer than either rubidium or lithium, with a crustal abundance of only 3 ppm. Cesium does not substitute for potassium as readily as rubidium and is present in much lower concentrations within potassium aluminosilicate. The mineral beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$) can contain percent levels of cesium. Cesium, like lithium can occur within pegmatites. Cesium is also relatively enriched within felsic igneous rocks.

2.3.2 Distribution at the Site

The rare alkali metals could be relatively enriched within felsic rocks present at ARWW&S such as the Boulder Batholith. Although pegmatites are known to exist in the area, none are known to be rich in rare alkali metals. Lithium and rubidium may be present within clay minerals present within the aquifer at the site.

Lithium occurs in some non-Montana hot springs at concentrations on the order of 7-8 mg/L. For Montana hot springs, concentrations are an order of magnitude lower (0.100.70 mg/L). Rubidium is not often analyzed and analyses for other hot spring waters were not available for this evaluation. Cesium is relatively higher within the Warm Springs and Fairmont systems relative to most of the hot springs in Montana, which are <0.10 mg/L (**Table 2-5**).

Table 2-5 – Summary of Rare Alkali Metal Occurrence in Waters

Water	Lithium (ppm)	Rubidium (ppm)	Cesium (ppm)
Brines			
Great Salt Lake ¹	18-64	-	-
Salton Sea ¹	100-400	-	-
Searles Lake, CA ¹	54-60	-	-
Geothermal Springs			
Steamboat Springs, CO ¹	7.1	-	-
Steamboat Springs, NV ¹	7.6	-	-
Yellowstone ¹	8.4	-	-
Alhambra Hot Springs ²	0.32	-	<0.1
Boulder Hot Springs – a ²	0.22	-	<0.1
Boulder Hot Springs – b ²	0.24	-	<0.1
Pipestone Hot Springs ²	0.09	-	<0.1
Warm Springs Hospital	0.4	0.155	0.110
Fairmont Springs	0.5-0.7	0.019-0.24	0.068-0.071
Geyser Gulch ²	0.213-0.215	0.086-0.087	0.027 -0.030-
Other			
River water ³	0.0011-0.0020	0.00011-0.0015	-

1. Garrett, 2004
2. USGS, 1976
3. Hem, 1985

The rare alkali metals are relatively enriched in leachate from cores taken in the Fairmont area English Gulch (except Li), and Crackerville (Li only) (**Table 2-6**). However, there is a lot of scatter in the data. Some rare alkali metals are high, some low and others in between. The only correlations with arsenic are for Cs and Rb. These appear to be for English Gulch 41 m, which has the highest leachate concentrations of all of the samples for As, Rb, and Cs.

Table 2-6 - Arsenic and Rare Alkali Metal SPLP Leaching Results¹

Rock Sample	Type	As	Cs	Li	Rb
English Gulch (RW)	Rock	9051.99	13.99	<15	31.83
Crackerville (FR)	Rock	522.03	<0.1	9.99	<0.1
Tlcl Breccia	Rock	12.64	<0.1	3.83	1.96
Crackerville (FR)	Rock	4.82	<0.1	10.42	1.69

Table 2-6 - Arsenic and Rare Alkali Metal SPLP Leaching Results¹

Rock Sample	Type	As	Cs	Li	Rb
English Gulch (RW)	Rock	55.1	0.23	<1.5	2.13
English Gulch (RW)	Rock	20.37	<0.1	<1.5	0.6
Fairmont (SH)	Rock	15.15	0.98	13.03	0.79
Fairmont (SH)	Rock	8.3	2.9	121.77	2.01
Kg-Granite weathered	Rock	17.24	<0.1	8.06	2.55
Tlcl Apanitic	Rock	0.69	<0.1	2.91	0.75
Tlcl Lava	Rock	0.89	<0.1	3.25	0.33
Tlcp Porphyry	Rock	18.66	<0.1	2.14	1.08
Tlcw Welded Tuff	Rock	12.77	<0.1	3.87	0.69
Tuxedo Mine Red-black breccia	Rock	0.45	0.34	4.47	5.09
Tuxedo Mine yellow-gray breccia	Rock	2.31	2.96	4.71	24
Crackerville (FR)	Sediment	14.57	<0.1	9.3	0.97
Fairmont (SH)	Sediment	0.87	1.25	<1.5	3.02
Powell Vista (MS)	Sediment	7.48	<0.1	<1.5	1.16
Powell Vista (MS)	Sediment	19.6	<0.1	26.28	1.52
Powell Vista (MS)	Sediment	16.02	<0.1	2.23	2.56
Crackerville (FR)	Soil	118.59	<0.1	8.34	0.7
English Gulch (RW)	Soil	89.08	<0.1	<1	0.48
Fairmont (SH)	Soil	218.14	<0.1	<1.0	0.22
Fairmont (SH)	Soil	220.37	<0.1	<1.0	0.26
Fairmont (SH)	Soil	221.88	<0.1	2.91	0.26
Powell Vista (MS)	Soil	448.91	<0.1	<1.0	1.29
Soil near Flint Creek Area	Soil	185.4	<0.1	3.29	0.51
Soil near MW-229	Soil	106.41	<0.1	3.8	1.9

1. MBMG (2013) Tables 7 and 8

Plots of As vs. Li and As vs. Rb (using ½ the detection limit for <DL values) are presented in Figures 2-7a/2-7b and 2-8a/2-8b, respectively.

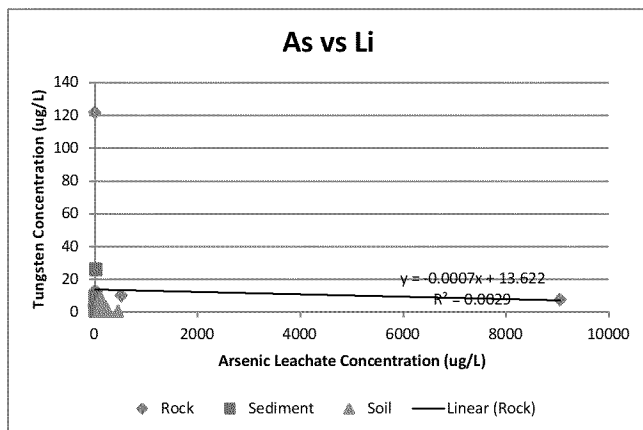


Figure 2-7a - As vs Li in SPLP leachate (all samples).

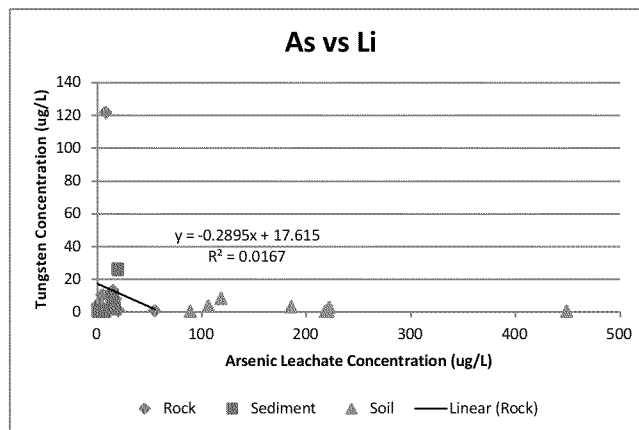


Figure 2-7b - As vs Li in SPLP leachate (without English Gulch 41 m or Crackerville 118 m).

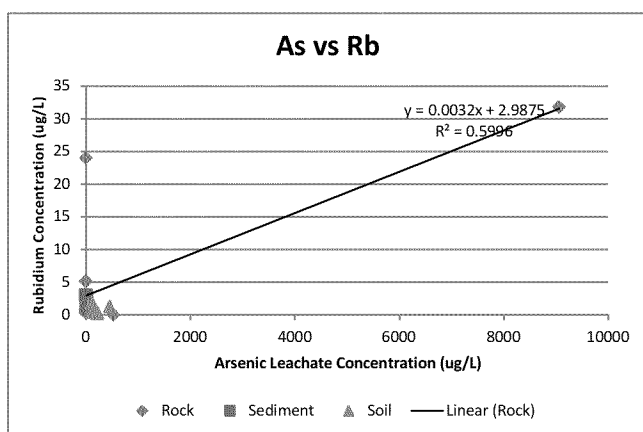


Figure 2-8a - As vs Rb in SPLP leachate (all samples).

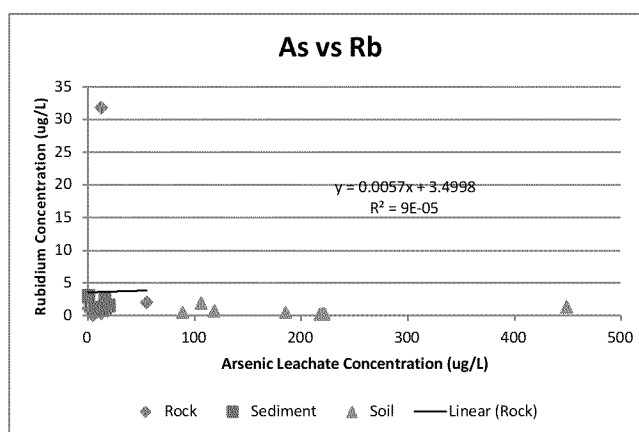


Figure 2-8b - As vs Rb in SPLP leachate (without English Gulch 41 m or Crackerville 118 m).

The correlations for between As and Li and between As and Rb were quite poor, with R values well under 0.1. A plot of As vs Cs was not constructed due to the high frequency of nondetect results.

Plots of Li and Rb vs. As for ground water with As < 50 $\mu\text{g/L}$ are shown in Figure 2-9.

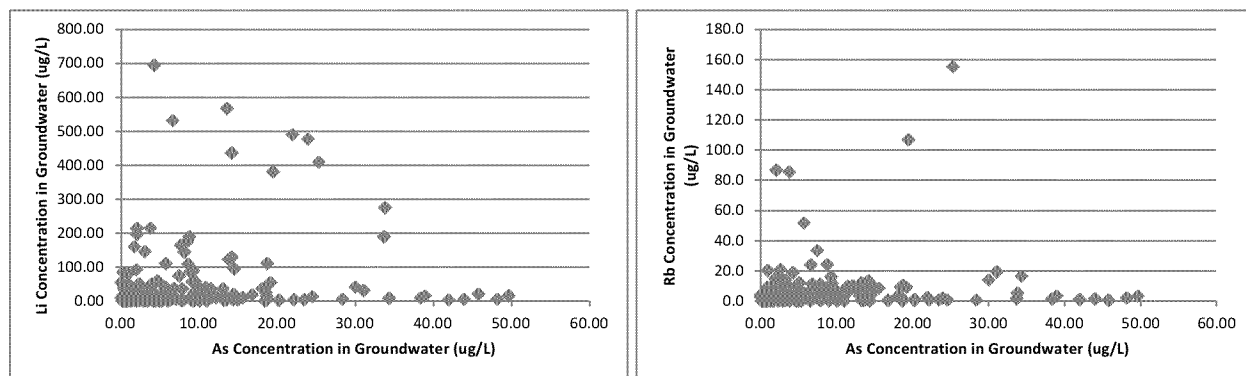


Figure 2-9 - As vs Li and Rb concentrations in site groundwater (limited to As < 50 µg/L).

No correlation exists between As and either Li or Rb.

2.4 Conclusions

Five of the trace elements which have been identified by AR as important for distinguishing the source of arsenic at the ARWW&S site (W, B, Li, Rb, and Cs) have been evaluated using data from the literature and the MBMG DSR report. These trace elements have multiple potential sources at the site, some containing arsenic and others with little or no arsenic, including:

- Leaching of volcanic and granitic rocks and associated hydrothermal veins
- Leaching of pegmatites (known to be associated with the Boulder Batholith)
- Non-smelter related anthropogenic sources, including fertilizer (W) and coalburning stack emissions (B and possibly As)
- Geothermal water

The only source of these trace elements which also contains significant arsenic is the hydrothermal veins. The geothermal waters at the ARWW&S site are low in arsenic (<30 µg/L). MBMG's leaching study showed that important arsenic leaching of mineralized bedrock is limited to a few isolated areas which were acknowledged within the Agency's Interpretive Report.

The multiple sources of the five trace elements evaluated have resulted in a random distribution of these elements both spatially and with respect to arsenic concentrations.

Section 3

Smelter Fallout Evaluation

3.1 Vegetation Contamination

Figure 3-1 shows arsenic in vegetation samples (parts per million; ppm) collected during the period of intense smelter fallout from 1902 to 1907. The locations are not precise, but are the best available from the original source (Swain and Harkins 1908). Background locations 75 and 100 miles from Anaconda were reported with a concentration of zero. Three samples from the Garison vicinity ranged from 21 to 35 ppm. The researchers noted that the arsenic in the vegetation was from direct fallout and not taken up from the soil.

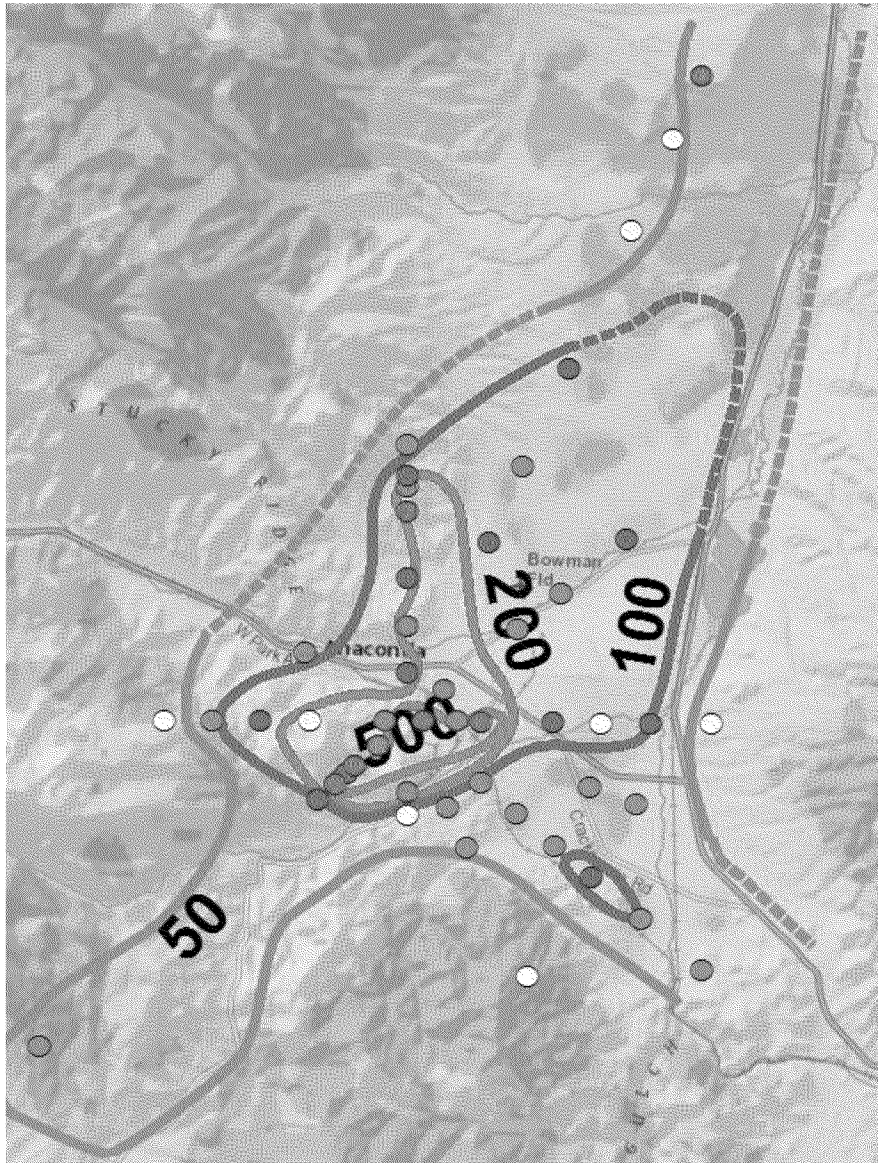


Figure 3-1: Arsenic in Vegetation (ppm) from Smelter Fallout 1902-1907.
Source of data points: Swain and Harkins 1908.

source of arsenic in the plants. *"The results admit of only one interpretation, which is that the smelter smoke is the source of the arsenic found in such excessive amounts in the vegetation of the region about Anaconda"* (Swain and Harkins 1908).

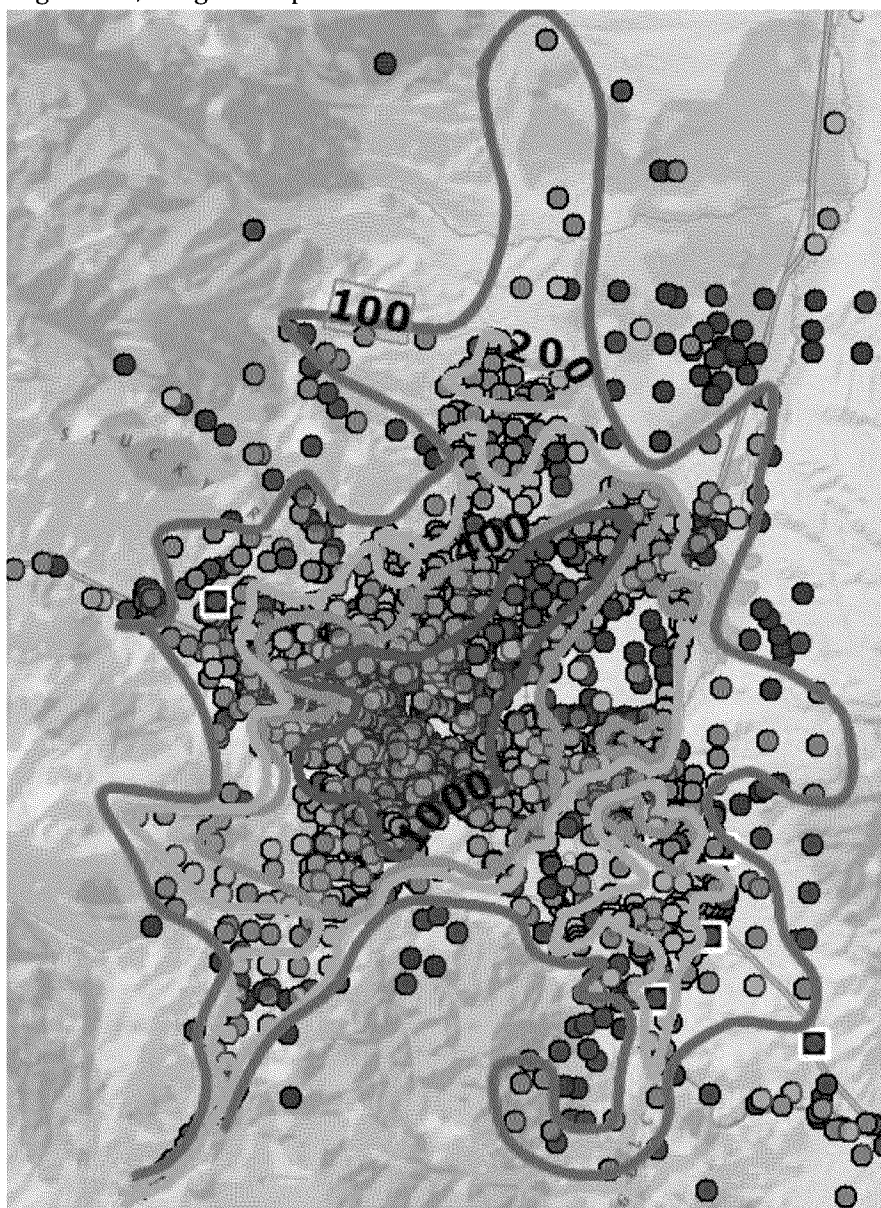
3.2 Surface Soil Contamination

The extent of arsenic impacts to surface soil in the ARWW&S OU has been investigated for many years resulting in thousands of points in the database. Multiple depth sampling has clearly shown that surface soil is more contaminated than subsurface soil indicating a smelter source for the arsenic. This does not apply to areas of discrete wastes.

A description of the extent of smelter smoke was provided based on direct observations of the researchers: *"Pouring out of the stack a thousand feet above the valley floor, the smoke stream can be traced as far as the eye can reach in that normally clear atmosphere, trailing down the valley for thirty miles toward Garrison, or often eastward in the direction of Butte, or sweeping over into Mill Valley and filling the narrow ravines which lead down from the Continental Divide, fourteen miles to the south."* (Swain and Harkins 1908) The general pattern of arsenic in vegetation matches the description of smoke extents.

Some soil and dust sampling was also conducted, but too few locations were samples to generate a meaningful map of the extent of fallout. Instead, the soil and dust samples were used to determine the

Figure 3-2 shows the extent of arsenic in surface soil samples from CERCLA investigations. Similar to Figure 3-1, the general pattern is that elevated arsenic concentrations extend northward toward



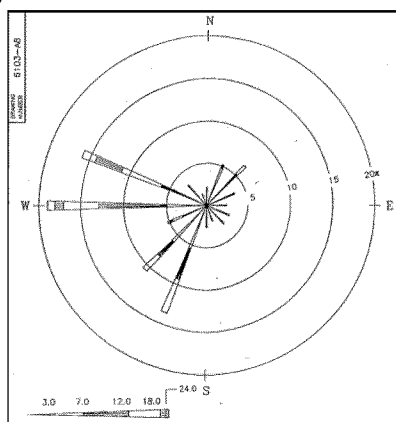
Garrison, southeastward to Crackerville, and southwesterly to California Creek.

There is an apparent correlation between the extent of arsenic in vegetation from smelter fallout and arsenic in soil 100 years later. The distribution of smoke was strongly influenced by wind and topography. Much of the arsenic has impacted valley areas near the Washoe smelter stack. The impacts further from the stack to the north, southwest, and southeast are probably due to a combination of wind and topography. Figure 3-3 shows a wind rose from the vicinity of the smelter. Wind commonly blows to the east and southeast toward Crackerville and to the northeast toward Deer Lodge. Lesser winds are evident to the southwest

Figure 3-2: Arsenic in Surface Soil (ppm) 1980s to present. Source: CERCLA data.

toward California Creek. The topography toward Crackerville and California Creek forms passes between mountains and likely funneled the wind and smelter smoke in these areas. Northward, the valley is wide allowing distribution of smoke throughout the valley.

Figure 3-3: Wind Rose from the ARW&W RI



NOTE: Diagram of the frequency of occurrence for each wind direction. Wind direction is the direction from which the wind is blowing. For example: Wind is blowing from the north 2.2 percent of the time.

Source: MMA, 1991

From: Titan Environmental, Windrose
Site 4 - Zinc Processing Area
Period: 7/90 through 6/91

3.3 Previous TI Evaluations

The bedrock aquifer TI evaluation (EPA 1996), the first addendum (EPA and MDEQ 1998a) and the second addendum to the bedrock aquifer TI evaluation (EPA 2011a) identified extensive areas of bedrock ground water contamination by arsenic and attributed the source to widespread soil contamination caused by smelter emissions. The initial TI evaluation and the first addendum resulted in waiver of the arsenic human health standard of 18 $\mu\text{g/L}$ in the ARWW&S ROD (EPA and MDEQ 1998b). The second addendum revised the extent of contamination based on a lower arsenic standard (10 $\mu\text{g/L}$). Subsequently, the arsenic standard for ground water was waived for a larger area in the 2011 ROD amendment (EPA and MDEQ 2011).

Based on these evaluations, bedrock ground water impacts due to smelter fallout are documented at least 10.2 miles to the south and 10.9 miles to the north of the Washoe smelter stack. In the bedrock aquifer areas, the primary recharge is local with minimal dilution from upgradient sources. This suggests that bedrock ground water within the Bedrock TI Zone should correlate with the extent of leachable arsenic in soil. This is the case to the north (west of the alluvial valley) and southwest. This has not been confirmed to the southeast in the Flint Creek area due to the lack of spring, monitoring well, and spring-fed tributary data available during development of the Bedrock Aquifer TI Evaluation Addenda and Spring-Fed Tributary TI Evaluation.

Alluvial ground water is subject to dilution from upgradient sources, but water table monitoring wells and seeps often reflect local recharge. In the North Opportunity TI Evaluation (EPA 2011b), elevated arsenic was found in untilled soil samples extending to the edge of the OU boundary to the northeast. Corresponding elevated arsenic in shallow ground water was found along this same trend as far as 10.6 miles from the Washoe smelter stack. Soil and alluvial ground water contamination may exist beyond 10.5 miles, but the investigation did not include the adjacent operable unit.

Based on the findings of these three TI evaluations, groundwater contamination from infiltration of precipitation through soil contaminated by smelter fallout was documented to exist greater than 10 miles from the stack in three directions (see Figure 3-4). This is significantly farther than the 6 mile

limit claimed in the AR statistical report which was based on a much smaller data set than that used in the TI evaluations. Considering the findings of the TI evaluations, it would be reasonable to consider that ground water impacts from smelter fallout are possible or likely within 10 miles of the stack in downwind directions where topography would not impede the movement of smelter emissions.

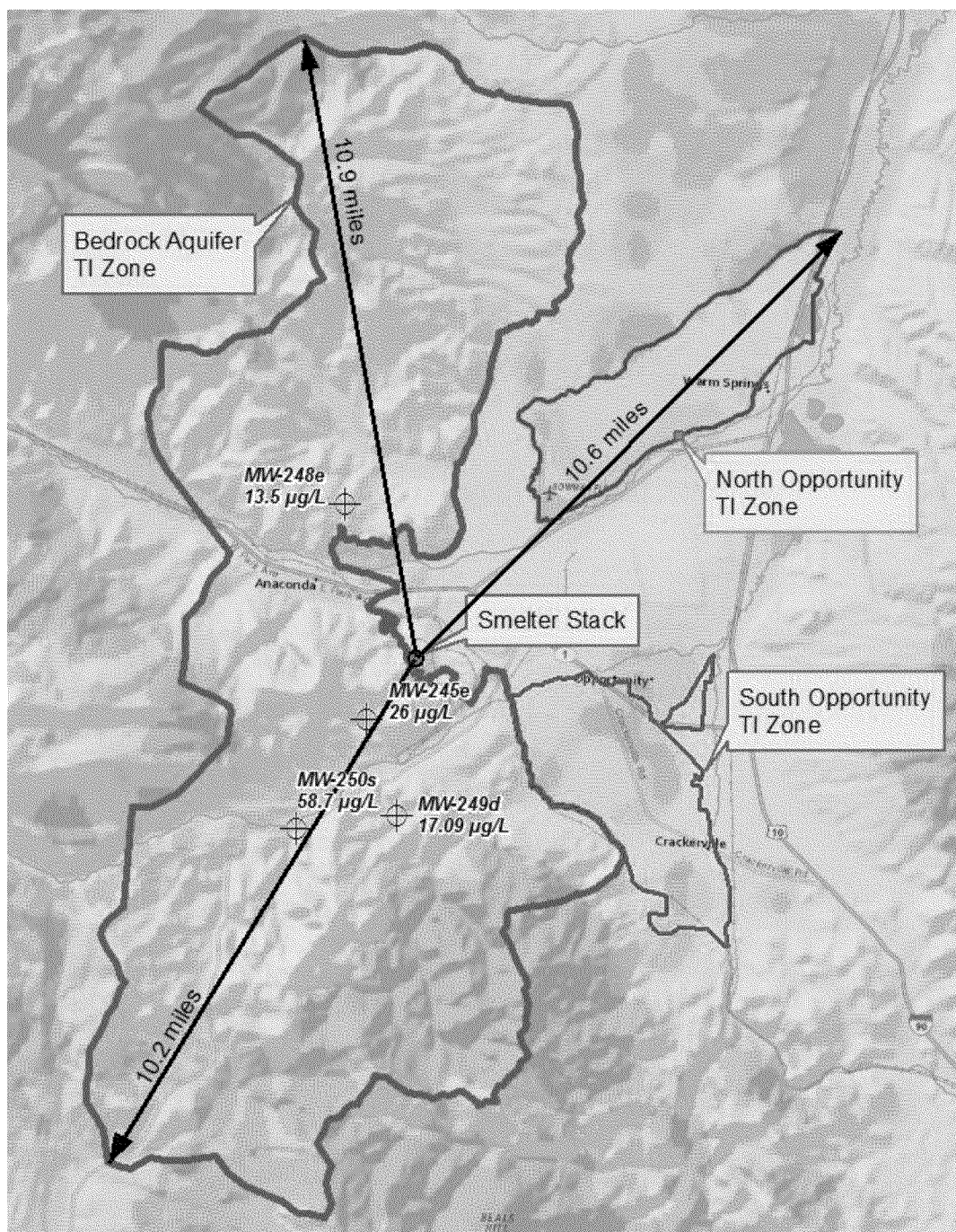


Figure 3-4: Ground Water TI Zones

3.4 Vertical Extent of Ground Water Contamination

The AR Statistical Report indicates that ground water contamination from smelter impacts is limited to 35 feet below ground surface. The First Addendum to the Bedrock TI Evaluation established the maximum depth of ground water contamination based on an arsenic standard at the time of 18 µg/L to be 250 feet. This was based on springs and monitoring well pairs and triplets that were drilled on Stucky Ridge (SP97-20, MW-248s, MW-248d, and MW-248e), Smelter Hill (MW-245s, MW-245d, and MW-245e), Cabbage Gulch (SP98-36, MW-249s and MW-249d), and Joyner Creek areas (SP98-37, MW-250s, and MW-250d). These locations are shown on Figure 3-4.

The Second Addendum updated the data based on an arsenic standard of 10 µg/L and confirmed the depth of 250 feet. The maximum known depth of arsenic ground water contamination on Stucky Ridge 3.0 miles from the stack is 182 feet. In Joyner Creek, the maximum depth of arsenic ground water contamination 3.6 miles from the stack is 63 feet below ground surface. The maximum depth of known arsenic contamination in Cabbage Gulch 2.7 miles from the stack is 201 feet below ground surface. On Smelter Hill closer to the stack, several wells indicated contamination more than 100 feet deep with the maximum known depth of ground water contamination at 247 feet resulting in confirmation of the depth of the Bedrock TI Zone at 250 feet (EPA 2011a). Clearly, ground water contamination extends much deeper than 35 feet. The wells used in the Bedrock Aquifer TI evaluation were in upland areas considered to have soil contaminated solely by smelter emissions fallout with no potential impacts by discrete waste sources such as tailings. Therefore, impacts to ground water from smelter emissions fallout are known to extend to at least 201 feet below ground surface 2.7 miles south from the stack at Cabbage Gulch, 63 feet below ground surface 3.6 miles southwest from the stack at Joyner Creek, and 182 feet below ground surface 3.0 miles northwest from the stack at Stucky Ridge (see Figure 4).

3.5 Conclusions

The extent of arsenic in vegetation, soil, and ground water all demonstrate a similar geographic pattern indicating that all are related and are a result of smelter fallout. Impacts to ground water from smelter fallout are documented in the TI evaluations to extend greater than 10 miles from the smelter stack in three directions. The depth of ground water contamination due to smelter fallout is greater than 200 feet in some locations. These findings are based on a much more robust data set than was used in the AR Statistical Report (Atlantic Richfield 2013) and are documented in EPA reports (EPA 1996; EPA and MDEQ 1998a; EPA 2011a, EPA 2011b) reviewed and approved by EPA headquarters.

Section 4

Summary

At the request of EPA, this Addendum to the Agency Interpretive Report for MBMG's ARWW&S Arsenic Source Investigation Final Project Data Summary Report was prepared to address comments from AR that CDM Smith failed to use trace element data in their evaluations presented in the interpretive report, and consequently AR's proposed limit of smelter emissions impacts to ground water was less than six miles from the stack and limited to a depth of 35 feet below ground surface.

Section 2 of this addendum presents the analysis of trace elements tungsten (W), boron (B), lithium (Li), rubidium (Rb) and cesium (Cs). The analysis demonstrates that there are multiple low level sources of these trace elements at the site, which are localized in terms of their extent. Arsenic concentrations above the performance standard of 10 mg/l associated with some of these trace elements is limited to hydrothermal veins at English Gulch, Crackerville Deep, and geothermal waters at the Warm Springs area. There was no evidence of widespread trace element distribution that correlated to the arsenic TI zones currently delineated by the existing data.

Section 3 of this addendum summarizes the existing arsenic data distribution for vegetation, soils, and ground water as they relate to smelter stack emissions and inferred deposition for the nearly 100 years (late 1880s to 1980) of copper smelting operations which occurred at the site. The similarity shown in these arsenic distributions provides a line of evidence that confirms that smelter emission deposition is the primary source of arsenic concentrations in the TI zones as presented in the 2011 ARWW&S OU Record of Decision Addendum. Further review of this existing data suggests that arsenic impacts from the smelter may extend to a depth of 200 or more feet in some locations, and as far away as 10 miles from the Washoe smelter stack.

Section 5

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